Evolution of Microstructure and Grain Growth in $\text{ZrO}_2\text{-Y}_2\text{O}_3$ Alloys

Yu-ichi YOSHIKAWA and Taketo SAKUMA

Department of Materials Science, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113, Japan.

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The microstructure evolution and grain growth during high-temperature heat treatment in $\text{ZrO}_2\text{-4}$ and $8\text{mol}\%\text{Y}_2\text{O}_3$ alloys were examined. $\text{ZrO}_2\text{-8mol}\%\text{Y}_2\text{O}_3$ alloy was of single cubic phase ($c\text{-ZrO}_2$), while $\text{ZrO}_2\text{-4mol}\%\text{Y}_2\text{O}_3$ alloy consisted of mixed grains of $c\text{-ZrO}_2$ and tetragonal phase ($t\text{-ZrO}_2$) with the equilibrium yttria contents after a certain period of heating. This structure was different from the microstructure containing precipitates in grain interior, and was referred to be the dual-phase structure. The grain growth of dual-phase structure was much slower than that of single $c\text{-ZrO}_2$. The grain growth kinetics of dual-phase structure under the equilibrium partitioning of yttria between $c\text{-ZrO}_2$ and $t\text{-ZrO}_2$ grains could be described by the rate equation which was derived by assuming the growth of individual grains limited by grain-boundary diffusion of yttrium ions.

KEY WORDS: zirconia; microstructure; sintering; grain growth; dual-phase; cubic phase.

1. Introduction

Partially-stabilized zirconia (PSZ) or tetragonal zirconia polycrystals (TZP) is known as toughened zirconia ceramics.¹⁻⁶ The strength and toughness of these materials depend on various factors such as powder preparation, amount of cubic-stabilizing oxide, sintering temperature, soaking time and so on.⁷⁻¹¹ It is essential to fabricate the fully-dense and fine-grained PSZ or TZP with suitable composition for obtaining excellent mechanical properties. Therefore, the inhibition of grain growth is very important in sintering process. Lee and Chen have recently reported that the grain growth of $\text{ZrO}_2\text{-8mol}\%\text{Y}_2\text{O}_3$ ($c\text{-ZrO}_2$) was faster than that of $\text{ZrO}_2\text{-2mol}\%\text{Y}_2\text{O}_3$ ($t\text{-ZrO}_2$).¹² Lange *et al.* have found that the partitioning of Y_2O_3 between $c\text{-ZrO}_2$ and $t\text{-ZrO}_2$ suppresses the grain growth in $\text{ZrO}_2\text{-Y}_2\text{O}_3$ alloys.¹³ However, these experimental data has not quantitatively been understood yet.

In the present study, the grain growth during high-temperature annealing was examined in $\text{ZrO}_2\text{-4}$ and $8\text{mol}\%\text{Y}_2\text{O}_3$ alloys, and the grain growth kinetics was discussed in detail.

2. Experimental Procedures

The starting materials used were hydrolyzed zirconia powders containing 4 and 8 mol% Y_2O_3 which were supplied by Tosoh Co. Ltd. The average diameter of original powders was about 25 nm. These powders were pressed into bars in cemented carbides die under a pressure of 100 MPa. They were pre-sintered at 1350°C for 2 h, and then heated isothermally in a temperature range between 1600 and 1800°C in air. X-ray diffraction (XRD) studies were carried out by Mac Science MXP-18 using copper target. The bulk density of the presintered body

was measured by the Archimedes technique. Metallographic examinations were made by optical microscope for polished and thermally etched specimens, and by transmission electron microscope (TEM), HITACHI H-800, operated at 200 kV for thin foils made by ion milling. Grain size was measured by linear intercept method. Analytical electron microscope JEOL 2000FX equipped with X-ray energy dispersive spectrometer (EDS) was used to analyze the yttria content of microarea in the order of 100 nm².

3. Results

3.1. Microstructures

Fig. 1 shows the microstructures of presintered $\text{ZrO}_2\text{-(a) 4mol}\%\text{Y}_2\text{O}_3$ and $\text{-(b) 8mol}\%\text{Y}_2\text{O}_3$ alloys. The grain size is much smaller in $\text{ZrO}_2\text{-4mol}\%\text{Y}_2\text{O}_3$ alloy than in $\text{ZrO}_2\text{-8mol}\%\text{Y}_2\text{O}_3$ alloy; the average grain size of these alloys was about 0.3 and 2 μm , respectively. Twin-like contrast and unidentified contrast are seen in some grains in Fig. 1(a), while each grain is almost featureless except for bend contours in Fig. 1(b). Pores on grain boundaries are only seen in Fig. 1(b). This fact is in accord with the density data of presintered alloys; more than 99 % of theoretical density in $\text{ZrO}_2\text{-4mol}\%\text{Y}_2\text{O}_3$ alloy and about 97 % in $\text{ZrO}_2\text{-8mol}\%\text{Y}_2\text{O}_3$ alloy.

Fig. 2 shows the microstructure of $\text{ZrO}_2\text{-4mol}\%\text{Y}_2\text{O}_3$ alloy heated at 1700°C for 10 h, where figures show the yttria content of each grain estimated by EDS analysis. Some grains have yttria content around 2 mol%, while others around 5.5 mol%. Most of the former grains are almost featureless in grain interior, but the latter ones ordinary have twin-like or lenticular features. No precipitates are seen in both grains. The grain size was almost uniform

in this alloy irrespective of yttria content.

Fig. 3 is the result of EDS analysis in each grain of ZrO_2 -4mol% Y_2O_3 alloy. Grains with various yttria contents are present in presintered state (Fig. 3(a)). However, the yttria content in individual grains is separated into two groups, the one with about 2-3 mol% Y_2O_3 and another with 5-6 mol% Y_2O_3 after annealing at 1700°C for 10 h (Fig. 3(c)).

Fig. 1. Microstructure of presintered alloys at 1350°C for 2 h; ZrO_2 -(a) 4mol% Y_2O_3 , and -(b) 8mol% Y_2O_3 alloys. Note that the magnification of the two micrographs is different.

Fig. 2. Microstructure of ZrO_2 -4mol% Y_2O_3 alloy heated at 1700°C for 10 h. Figures in the micrograph show the yttria content in each grain.

Longer annealing at this temperature always resulted in the generation of these two groups of grains. As discussed later, this is caused by partitioning of yttria between grains. The partitioning must not be completed by annealing at 1700°C for 1 h (Fig. 3(b)). Such partitioning was not found in ZrO_2 -8mol% Y_2O_3 alloy, where the yttria content of individual grains was almost uniform around 8 mol%.

Fig. 4 is the X-ray intensity profiles in presintered and annealed alloys. The profiles of 2θ angles between 72 and 76° are shown in Fig. 4, because 400

Fig. 3. Histogram of yttria content in each grain in ZrO_2 -4mol% Y_2O_3 alloy. The heat treatment is (a) presintered at 1350°C for 5 h (b) heated at 1700°C for 1 h, and (c) 1700°C for 10 h

Fig. 4. X-ray diffraction intensity profiles of ZrO_2 - Y_2O_3 alloys; (1) presintered 4 mol% Y_2O_3 , (b) 4 mol% Y_2O_3 annealed at 1700°C for 100 h, (c) 8 mol% Y_2O_3 as sintered, and (d) 8 mol% Y_2O_3 annealed at 1700°C for 92 h.

type reflections are sensitive to distinguish tetragonal and cubic phases. Peaks from each reflection appear as pairs from Cu $K\alpha_1$ and Cu $K\alpha_2$ radiations. In $\text{ZrO}_2\text{-}4\text{mol}\%\text{Y}_2\text{O}_3$ alloy, the profiles are broad in presintered state (Fig. 4(a)), but they become more sharp due to subsequent annealing (Fig. 4(b)). These peaks may be identified to be of two tetragonal phases with different lattice parameters. One is $t\text{-ZrO}_2$ with a lattice parameter

$$a=0.510 \text{ nm}$$

$$c=0.518 \text{ nm}$$

and another is $t'\text{-ZrO}_2$ containing a higher yttria content whose lattice parameter is

$$a=0.512 \text{ nm}$$

$$c=0.516 \text{ nm}.$$

The latter one may be referred to as $t'\text{-ZrO}_2$.¹⁴⁾ Judging from the previous lattice parameter data in $\text{ZrO}_2\text{-Y}_2\text{O}_3$ alloys,^{17,18)} above lattice parameters correspond to tetragonal phase with yttria content 2 mol% for $t\text{-ZrO}_2$ and 6 mol% for $t'\text{-ZrO}_2$. The profiles in $\text{ZrO}_2\text{-}8\text{mol}\%\text{Y}_2\text{O}_3$ alloy can be identified to be of single $c\text{-ZrO}_2$ in presintered (Fig. 4(c)) and annealed (Fig. 4(d)) states.

3.2. Grain Growth during Annealing

It was observed that grains became larger during isothermal annealing at high temperatures. The microstructures of $\text{ZrO}_2\text{-}4\text{mol}\%\text{Y}_2\text{O}_3$ alloy annealed at 1700°C are shown in Fig. 5. The grain size increased fairly uniformly with an increase of annealing time.

Fig. 6 is the microstructure of $\text{ZrO}_2\text{-}8\text{mol}\%\text{Y}_2\text{O}_3$ alloy annealed at 1700°C for 10 h. The comparison of the grain size of the two alloys at the same heat treatment, Fig. 5(a) and Fig. 6, indicates that grains are much larger in $\text{ZrO}_2\text{-}8\text{mol}\%\text{Y}_2\text{O}_3$ alloy than in $\text{ZrO}_2\text{-}4\text{mol}\%\text{Y}_2\text{O}_3$ alloy.

Fig. 5. Optical micrographs of annealed $\text{ZrO}_2\text{-}4\text{mol}\%\text{Y}_2\text{O}_3$ alloy at 1700°C for (a) 10 h and (b) 72 h.

Fig. 7 shows the change in average grain size with annealing time at two temperatures. For comparison, the previous data at 1700°C obtained by Lee and Chen is also shown as broken line in Fig. 7. At each temperature, the grain growth occurs much faster in $\text{ZrO}_2\text{-}8\text{mol}\%\text{Y}_2\text{O}_3$ alloy than in $\text{ZrO}_2\text{-}4\text{mol}\%\text{Y}_2\text{O}_3$ alloy. According to the cubic-tetragonal equilibrium in $\text{ZrO}_2\text{-Y}_2\text{O}_3$ system, $\text{ZrO}_2\text{-}8\text{mol}\%\text{Y}_2\text{O}_3$ is in the single cubic phase region at the annealing temperature, while $\text{ZrO}_2\text{-}4\text{mol}\%\text{Y}_2\text{O}_3$ alloy is in the cubic-tetragonal two-phase region.^{17,19)} Fig. 7 indicates that the grain growth takes place much easily in the single phase region than in the two-phase region. The grain growth kinetics will quantitatively be discussed in the following section.

4. Discussion

4.1. Evolution of Microstructure

Evolution of microstructure in $\text{ZrO}_2\text{-}4\text{mol}\%\text{Y}_2\text{O}_3$ alloy during heat treatment is discussed in this section. During sintering or subsequent annealing in the $c\text{-}$

Fig. 6. Optical micrograph of $\text{ZrO}_2\text{-}8\text{mol}\%\text{Y}_2\text{O}_3$ alloy annealed at 1700°C for 10 h.

●, ○: The present data in $\text{ZrO}_2\text{-}4$ and $8\text{mol}\%\text{Y}_2\text{O}_3$ alloys, respectively
 ----: The data obtained by Lee and Chen¹²⁾

Fig. 7. A plot of average grain size as a function of annealing time; (a) 1800°C and (b) 1700°C .

$\text{ZrO}_2/t\text{-ZrO}_2$ two phase region, not only densification and grain growth but also partitioning of yttria take place in this alloy. Fig. 3 indicates that the annealing at 1700°C for 10 h is enough to complete the equilibrium partitioning, and further annealing results in the generation of mixed structure of fine $t\text{-ZrO}_2$ grains and $c\text{-ZrO}_2$ grains, which had nearly the equilibrium yttria contents. This type of microstructure is often referred to be "dual-phase" or "duplex structure" in steels for distinguishing from usual precipitation structures.^{18,19)} On the other hand, it has been reported that coarse $c\text{-ZrO}_2$ grains containing $t\text{-ZrO}_2$ precipitates were sometimes developed in some yttria partially-stabilized zirconia (Y-PSZ) together with fine $t\text{-ZrO}_2$ grains.^{20,21)} Microstructure of Y-PSZ may be dependent on various factors such as powder preparation, sintering condition, etc. Thus, it is not possible to explain why coarse-grained $c\text{-ZrO}_2$ was formed in some Y-PSZ. However, it seems to be reasonable that the dual-phase structure is induced in fine-grained Y-PSZ during annealing in the two-phase region by the following reason. The average diffusion distance of cations $\bar{z}$ during the annealing at 1700°C for 10 h can roughly be estimated from their diffusion coefficient D_c as

$$\bar{z} \approx \sqrt{D_c t}.$$

By substituting the reported value of D_c at 1700°C

$$D_c = 2.4 \times 10^{-16} \text{ m}^2/\text{s},^{22)}$$

one can obtain

$$\bar{z} \approx 2.9 \text{ } \mu\text{m}.$$

This value is very close to the average grain size of $\text{ZrO}_2\text{-4mol}\%\text{Y}_2\text{O}_3$ alloy at this annealing, which is about 3.0 μm . This fact may indicate that the dual-phase structure is formed by partitioning of relevant ions when the average diffusion distance of the ions is in the order of average grain size.

It seems reasonable that $\text{ZrO}_2\text{-4mol}\%\text{Y}_2\text{O}_3$ alloy consisted of $t\text{-ZrO}_2$ and $c\text{-ZrO}_2$ grains at the annealing temperature as expected from the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ phase diagram. However, this alloy was made of $t\text{-ZrO}_2$ and $t'\text{-ZrO}_2$ at room temperature (Fig. 4). The yttria contents estimated from lattice parameters, 2 and 6 mol% as mentioned before agree with the result of microanalysis in Fig. 3, and are close to the equilibrium yttria contents of the two phases. This experimental evidence means that the high-temperature $t\text{-ZrO}_2$ is retained at room temperature, but $c\text{-ZrO}_2$ is transformed into $t'\text{-ZrO}_2$ during cooling after the annealing. It was confirmed by electron microscopy that the grains containing around 5.5 mol% Y_2O_3 have twins or lenticular microstructures. These microstructures are characteristic of $t'\text{-ZrO}_2$ formed by the diffusionless cubic-to-tetragonal ($c\text{-}t$) transition. According to the recent studies on the diffusionless $c\text{-}t$ transition,^{14,16,23-26)} this transition has a nature, which is always completed during cooling. For example, arc-melted alloys with yttria contents 3-7 mol% are fully tetragonal, while $\text{ZrO}_2\text{-8mol}\%\text{Y}_2\text{O}_3$ is of $c\text{-ZrO}_2$

only.^{16,24)} It can be expected from this result that high-temperature $c\text{-ZrO}_2$ containing around 5-6 mol% Y_2O_3 was transformed completely into $t'\text{-ZrO}_2$ during cooling in present alloys. The fact that $c\text{-ZrO}_2$ was not identified by room-temperature XRD analysis, is likely to be originated from the nature of the diffusionless $c\text{-}t$ transition.

4.2. Grain Growth in Cubic Zirconia

The grain growth in single-phase ceramics with a fairly uniform grain size is usually treated by the rate equation of normal grain growth,^{27,28)}

$$\bar{d}^2 - \bar{d}_0^2 = 2M\gamma V_m t \quad \dots\dots\dots(1)$$

where, $\bar{d}_0$: the average grain size at the time 0

M : the grain boundary mobility

V_m : molar volume

γ : the surface energy.

Fig. 8 shows a plot of $\bar{d}^2$ against t in $\text{ZrO}_2\text{-8mol}\%\text{Y}_2\text{O}_3$ alloy at three temperatures. From the slope of straight lines in Fig. 8, the values of M were calculated. These values are shown by open circles in Fig. 9, where γ and V_m were assumed to be 0.5 J/m² and 2×10^{-5} m³/mol, respectively. The experimental data in $c\text{-ZrO}_2$ and $t\text{-ZrO}_2$ obtained by Lee and Chen is also plotted in Fig. 9.¹²⁾ Linear relationship is satisfied in all the data, and the present data is intermediate between the data on $c\text{-ZrO}_2$ and $t\text{-ZrO}_2$ by Lee and Chen.

The grain boundary mobility in pure matter is written as²⁷⁾

$$M^i = \frac{D^{gb}}{RT\delta} \quad \dots\dots\dots(2)$$

where, D^{gb} : the grain boundary diffusion coefficient of relevant ions

M^i : the intrinsic grain boundary mobility

δ : the grain boundary width.

The intrinsic grain boundary mobility calculated from Eq. (2) is shown by the straight line in Fig. 9, where reported value of D^{gb} was used²²⁾ and δ was assumed to be 1 nm. The value of M^i thus obtained is several order of magnitude larger than the experimental data. This type of result is very common in ionic crystals

Fig. 8. A plot of square of average grain size as a function of annealing time in $\text{ZrO}_2\text{-8mol}\%\text{Y}_2\text{O}_3$ alloy.

Fig. 9. Grain boundary mobility of cubic zirconia.

and oxide ceramics.²⁹⁾ Except for high-purity metals, the grain growth of single-phase materials occurs at a rate much slower than expected from the intrinsic grain boundary mobility. It has been pointed out that the grain growth is markedly retarded even by a very small amount of impurities.^{30,31)} In *c*-ZrO₂ which contains Y₂O₃ as solid solutions, the grain growth may be retarded by the solute drag of Y³⁺ ions.

4.3. Grain Growth in Dual-phase Zirconia

It is known that the grain growth in metallic alloys is much sluggish in dual-phase alloys than in single phase ones.^{18,19)} The present study clarified that the dual-phase zirconia (ZrO₂-4mol%Y₂O₃ alloy) had much smaller grain growth rate than cubic zirconia (ZrO₂-8mol%Y₂O₃ alloy). The growth kinetics of dual-phase zirconia may be described as follows.

Zener has shown that the maximum retarding force for grain boundary migration exerted by a spherical particle with a radius r_p is given by $\pi r_p \gamma$.³²⁾ Assuming that this retarding force is equal to the driving force for grain boundary migration, then one can obtain the following relationship,

$$\frac{R_{\text{net}}}{r_p} = \frac{4}{3f} \quad \text{.....(3)}$$

where f is the volume fraction of second phase. The parameter R_{net} is the net radius of curvature, which is given by

$$\frac{1}{R_{\text{net}}} = \frac{1}{\rho_1} + \frac{1}{\rho_2} \quad \text{.....(4)}$$

where ρ_1 and ρ_2 are the radius of curvature of two grains in contact at the grain boundary. By taking R_{net} as the average grain size, the following relation is derived,

$$\frac{\bar{d}}{r} = \frac{4}{3f} \quad \text{.....(5)}$$

This is the equation usually referred to be the Zener's relation. It has later been clarified that Eq. (5) overestimates the total retarding force, and is modified by various workers.³³⁻³⁶⁾ The most probable relation, which agrees with various experimental data, may be³⁵⁾

$$\bar{d} = \frac{8r_p}{9\phi f} \quad \text{.....(6)}$$

where ϕ is the parameters including two factors; one is the angle between grain boundary and particle surface, and another is the factor depending on the radius of curvature of the grain boundary and the particle radius. When Eq. (6) is satisfied between the two phases and the grain growth is controlled by the Ostwald ripening of minor phase particles, the following rate equations can be derived,^{18,19,37-41)}

Volume-diffusion controlled case:

$$\bar{d}^3 - \bar{d}_0^3 = \left(\frac{8}{9\phi f} \right)^3 \frac{8\gamma V_m^\beta D_B x_B}{9RT(x_B^\beta - x_B^\alpha)^2} t \quad \text{.....(7)}$$

Grain boundary-diffusion controlled case:

$$\bar{d}^4 - \bar{d}_0^4 = \left(\frac{8}{9\phi f} \right)^4 \left(\frac{3}{4} \right)^3 \frac{2\gamma V_m^\beta \delta D_B^{gb} x_B^{gb}}{RT(x_B^\beta - x_B^\alpha)^2} t \quad \text{.....(8)}$$

where the α and β phases are taken to be the major and minor phases in dual-phase structure. The symbols D_B and D_B^{gb} are the volume and grain-boundary diffusion coefficients of B , and x_B is the solubility of each phase. In the present alloy, the major and minor phases were regarded to be *c*-ZrO₂ and *t*-ZrO₂, respectively, and B is Y³⁺ ions.

Fig. 10 is the log-log plot of experimental data at 1700°C. The data is represented by a straight line, whose slope is about 1/4. This result agrees with the grain growth data in ZrO₂-Al₂O₃.⁴²⁾ This fact may support the grain-boundary diffusion controlled growth as expected from Eq. (8). However, the slope is not so accurately decided in the log-log plot. It is more reliable to compare the experimental growth rate with the theoretical one for elucidating the controlling mechanism. For the theoretical calculation, there are no data on interfacial energy and grain boundary enrichment ratio of solute in ZrO₂-Y₂O₃ alloys. The interfacial energy of most of solids is known to be in the range between 0.1 and 1 J/m²,⁴³⁾ and so this energy was assumed to be 0.5 J/m². The number of experimental data on metallic alloys suggests that the grain boundary enrichment ratio of solute is related to solid solubility.⁴⁴⁾ On the basis of the reported relationship,⁴⁴⁾ the grain boundary enrichment ratio is tentatively taken to be 2, i.e.,

$$x_Y^{gb} = 2x_Y^{c\text{-ZrO}_2}$$

Other parameters were chosen from the data of the *c*-ZrO₂/*t*-ZrO₂ equilibrium,^{15,17)} and from the diffusion data in *c*-ZrO₂.²²⁾

Fig. 11 is the comparison between experimental

Fig. 10. A log-log plot of grain growth data in ZrO_2 -4mol% Y_2O_3 alloy at 1700°C.

-----: The calculated growth rate by Eq. (7)
 -----: The rates by Eq. (8)

Fig. 11. Grain growth rate of dual-phase structure in ZrO_2 -4mol% Y_2O_3 alloy at (a) 1800°C and (b) 1700°C.

data and growth rates calculated from Eqs. (7) and (8) at two temperatures. The growth rates expected from volume-diffusion controlled mechanism are much smaller than those from grain-boundary diffusion controlled mechanism at the two temperatures. The experimental data agrees with the grain-boundary diffusion controlled growth within a factor of two. Taking into account the ambiguities of various parameters used for the calculation, it seems reasonable that the grain growth of dual-phase ZrO_2 -4mol% Y_2O_3 alloy after the equilibrium partitioning is limited by the two phases which have different Y_2O_3 content and is expressed by the growth of each-phase grains due to the diffusion of yttrium ions along grain boundaries.

5. Conclusion

The microstructure and grain growth were examined during high-temperature annealing in ZrO_2 -4 and 8mol% Y_2O_3 alloys. The results obtained are as follows,

(1) The dual-phase structure was evolved during annealing in the c - ZrO_2 / t - ZrO_2 two-phase region in ZrO_2 -4mol% Y_2O_3 alloy, while single c - ZrO_2 grains were developed in ZrO_2 -8mol% Y_2O_3 alloy. In the dual-phase structure consisting of c - ZrO_2 and t - ZrO_2 grains, the equilibrium partitioning of yttria was attained during high-temperature annealing.

(2) The grain growth occurred much faster in ZrO_2 -8mol% Y_2O_3 alloy (c - ZrO_2) than in ZrO_2 -4mol% Y_2O_3 alloy (dual-phase). The development of dual-phase structure was effective for obtaining fine-grained structure.

(3) The grain growth rate in c - ZrO_2 was several order of magnitude slower than that expected from intrinsic grain boundary mobility. The solute-drag effect of yttria may retard the grain growth in c - ZrO_2 .

(4) The grain growth kinetics of dual-phase structure could satisfactorily be explained by the rate equation of fourth-power law, which was derived for growth of individual grains limited by grain boundary diffusion of yttrium ions.

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